A Molecular Dynamics Simulation of $CaSiO_3$ Melt Under an Electric Field *

HUANG Shi-Ping(黄世萍)[1], YOU Jing-Pin(尤静林)[1], JIANG Guo-Chang(蒋国昌)[1], F. Yoshida[2], XU Kuang-Di(徐匡迪)[1]

[1]*Shanghai Enhanced Laboratory of Ferro-metallurgy, Shanghai University, Shanghai 200072*

[2]*Department of Physics, Shiga University of Medical Science, Shiga 520-2192, Japan*

(Received 15 June 1999)

The results of a molecular dynamics (MD) simulation are presented for $CaSiO_3$ melt under an electric field. The two-body interaction potential is adopted in the simulation, with parameters chosen so that the calculated static structure is consistent with results of high temperature x-ray experiments. It is found that the MD results for the heat capacity at constant volume, the self-diffusion coefficient and the electrical conductivity change greatly when the electric field is over 500 MV/m. Discussion is given on these results, together with the frequency-dependent electrical conductivity.

PACS: 61.20.Ja, 61.20.Qg

Recently, much attention has been paid to silicate melts not only from a metallurgical point of view, but also from a petrosal perspective, with increasing curiosity for the earth's interior. The properties of $CaSiO_3$ melt have been studied along this line by x-ray and neutron diffraction studies.[1,2] These methods provide us with fundamental information on the structural features in the molten state. Molecular dynamics (MD) simulation are also valuable tools for studying the melt structure.[3,4] It is particularly useful to directly interpret dynamic behavior[5,6] on microscopic level.

In this paper we present the simulated results for $CaSiO_3$ melt under an electric field by using the constant volume molecular dynamics simulation, and discuss the structure and dynamic properties of the system.

The molecular dynamics simulation has been performed on a system of 1000 ions (600 O, 200 Ca and 200 Si). In the simulation the rigid-ion two-body potential is employed for $CaSiO_3$ melt. The interaction potential $\phi_{ij}(r)$ between atoms i and j is given by

$$\phi_{ij} = \frac{q_i q_j}{r_{ij}} + A_{ij}\exp(-\frac{r_{ij}}{\rho_{ij}}) - \frac{c_{ij}}{r_{ij}^6}. \qquad (1)$$

It consists of the long-range Coulomb part and the short-range repulsion part, with q_i being the charge of the ion i, r_{ij} the inter-ionic distance, ρ_{ij} the effective hardness and C_{ij} the dispersion parameter. The potential parameters developed by Matsui[7] are modified, the Ca ion size is increased to 0.1275 nm (Ref. 8) and the parameter (ρ_{ij}) is adjusted to agree with the high temperature x-ray experiments of Waseda *et al.*[1] The parameters are listed in Table 1. In addition to the two-body potential, the electric field E (MV/m) is considered in the simulation, which produces the energy of the charges,

$$U_{\mathrm{q,ext}} = -\sum_i^N q_i r_i \cdot E.$$

The initial ionic positions are chosen randomly in a cubic box. The periodic truncated octahedral (PTO) and the Ewald method were used for taking the summation of the electrostatic interaction. The time step is set as 0.001 ps, and the temperature was controlled to be 5000 K for initial 2000 steps, then it is reduced to the set temperature (1873 K). It takes about 20 ps for the system to attain an equilibrium state, whereby the energy fluctuation was less than 0.2%. The mean square displacement and the correlation functions are calculated by taking the average over more than 20000 steps in the conventional energy-conserving run. All simulations were performed on the DEC-500 workstation.

The static structure of disordered system is usually described by the partial radial distribution function (RDF). It represents the probability of finding another atom from an origin as a function of the radial distance. Table 2 summarizes the static features obtained from the RDF for melts at 1873 K without electric field. These are compared with the results of the x-ray diffraction. It is found that the results of the MD simulation based on the modified potential parameters are in agreement with that of the x-ray diffraction,[1] while the coordination number of Si-Si is less than that of the experiment.

Fluctuations in the potential energy under different electric fields are directly related to the constant volume heat capacity by

$$C_v = \frac{\langle\phi^2\rangle - \langle\phi\rangle^2}{k_{\mathrm{B}}T} + \frac{3}{2}N_0 k_{\mathrm{B}}, \qquad (2)$$

where ϕ is the potential energy, k_{B} and N_0 are the Boltzmann and the Avogadro constants, respectively. The heat capacity at constant volume for $CaSiO_3$ melt is shown in Fig. 1. It is found that C_v remain almost a constant in the range of 0−500 MV/m, and then it increases rapidly. This implies that the significant change takes place in the thermodynamic properties of the system when electrical field is over 500 MV/m.

*Supported by the National Natural Sciences Foundation of China under Grant Nos. 59874016 and 59832080, the Shanghai Research Center for Advanced Materials under Grant No. 98JC14018, and Shanghai Sciences Foundation of Youth.

©by the Chinese Physical Society

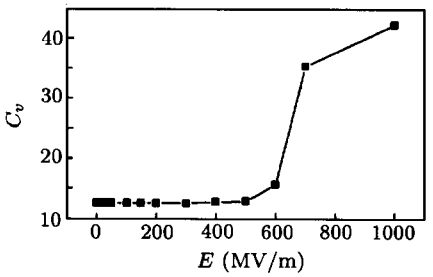


Fig. 1. Heat capacity at constant volume ($JK^{-1}mol^{-1}$) as a function of electric field.

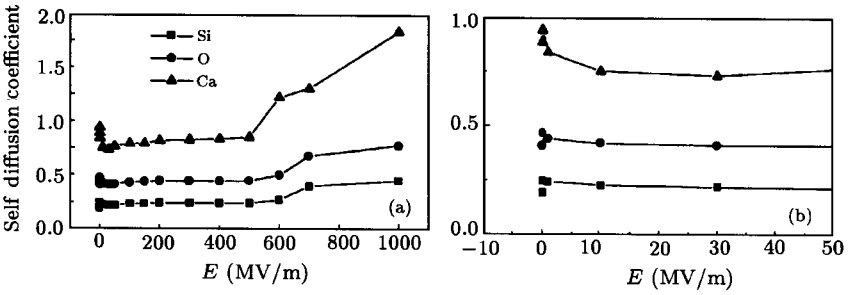


Fig. 2. Self-diffusion coefficient ($10^{-6}cm^2/s$) as a function of electric field (a) 0 to 1000 MV/m; (b) 0 to 30 MV/m.

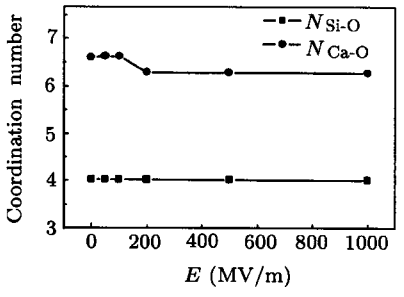


Fig. 3. Coordination number N_{Si-O} and N_{Ca-O} as functions of electric field.

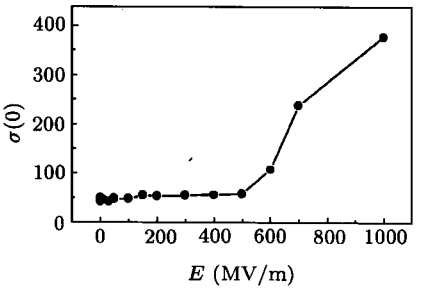


Fig. 4. Electrical conductivity ($\Omega^{-1}m^{-1}$) as a function of electric field.

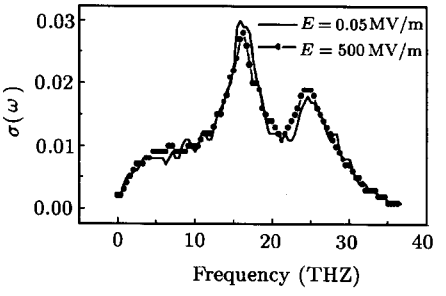


Fig. 5. Fourier transform of the charge current correlation function.

Table 1. Modified potential parameters for the molecular dynamics simulation run.

	q(e)	A_{ij}(eV)	ρ_{ij} (Å)	C_{ij}(eVÅ)[a]
O–O	$q_O = -1.298$	1621.734	0.300	30.22
Si–O	$q_{Si} = 2.329$	7363.700	0.190	0.00
Ca–O	$q_{Ca} = 1.565$	29353.157	0.210	0.00
Ca–Si		39991599.000	0.092	0.00
Ca–Ca		200790000.000	0.104	0.00
Si–Si		5006070.785	0.080	0.00

[a] From Ref. 6.

Table 2. Summary of static structure without electric field at 1873 K.

	MD simulation		X-ray diffraction[a]	
pair	r(nm)	N_{ij}	r(nm)	N_{ij}
Si–O	0.162	4.02	0.162	3.9
Ca–O	0.234	6.234	0.235	5.9
O–O	0.262	5.207	0.267	5.2
Si–Si	0.314	2.559	0.321	3.1
Ca–Si	0.350	5.739		
Ca–Ca	0.370	7.179		

[a] From Ref. 1.

The diffusion process can be studied by evaluating the mean square displacement of ion as a function of time. The self-diffusion coefficient can be calculated by the Einstein equation:

$$M(t) = \langle |r(t+s) - r(s)|^2 \rangle, \quad (3)$$

$$\lim_{t\to\infty} M(t) = 6\,Dt, \quad (4)$$

where t is a time interval during diffusion, and the angular bracket represents the ensemble average.

The calculated results for the self-diffusion is shown as a function of the electric field in Fig. 2. It is compared with experimental data[9,10] in Table 3. It is found that while the covalent contribution of Si–O is not considered in this potential model, our results agree with experiments in magnitude, except that the value of D_O is lager than the experimental data.

Table 3. Comparison of ionic transport coefficients by MD simulation and experimental data (molar fraction $x = 0.516$ in $(CaO)_x(SiO_2)_{1-x}$ melt)[b]

	MD simulation	Experiment
$D_{Ca}(10^{-5}cm^2/s)$	0.886	0.55
	0.735(E = 30 MV/m)	
$D_{Si}(10^{-5}cm^2/s)$	0.0191	0.011
$D_O(10^{-5}cm^2/s)$	0.040	0.013
$\sigma(\Omega^{-1}m^{-1})$	46.0 (E = 0.0 MV/m)	39.3
$\sigma(\Omega^{-1}m^{-1})$	41.3 (E = 0.05 MV/m)	

[b] From Refs. 9 and 10.

Figure 2(b) shows that the self-diffusion coefficient of ions increases with electric field ranging from 0 to 0.05 MV/m, but it decrease with further increase of the field. The effect of electric field on Ca ion is more sensitive than that on Si and O ions. When the electric field is over 500 MV/m, the self-diffusion coefficient increases rapidly. To examine the spatial arrangement of Si and O, the average coordination number N_{Si-O} and N_{Ca-O} are displayed as a function of electric field shown in Fig. 3. As we can see, the value of N_{Si-O} is about 4.0 in the whole range of the electric field. This fact means that the connectivity of the SiO_4 network appears marginally affected by Ca ion. It is consistent with the result that the RDF $g_{O-O}(r)$ shows the first peak at 0.262 nm, corresponding to the edge length of the SiO_4 tetrahedron. On the other hand, N_{Ca-O} shows a decrease in the range of 100–200 MV/m. This corresponds to the changes in the diffusion process of

Ca ion under electric field, as seen in Fig. 2.

The electrical conductivity σ is related to the normalized auto-correlation function of the total current $J_Z(t)$, defined as[11]

$$j_\alpha(t) = \sum_{i,\alpha} q_\alpha v_{i\alpha}, \tag{5}$$

$$C_{ZZ}(t) = \frac{1}{N}\langle j_\alpha(t) j_\alpha(0)\rangle, \tag{6}$$

$$J_Z(t) = \frac{C_{ZZ}(t)}{C_{ZZ}(0)}, \tag{7}$$

where $v_{i\alpha}$ and q_α are the velocity and mean ionic valence of species α, respectively. The usual electrical conductivity σ can be defined as[12]

$$\sigma = \lim_{\omega\to 0}\sigma(\omega) = \frac{\omega_p^2}{4\pi}\int_0^\infty J_Z(t)\mathrm{d}t, \tag{8}$$

$$\omega_p^2 = \sum_\alpha \frac{4\pi n_\alpha q_\alpha^2 e^2}{m_\alpha}, \tag{9}$$

where m_α and n_α are the mass and number density of α species, respectively. The electrical current correlation function shows a collective property of the system. To calculate a reliable value for the electrical conductivity σ, long runs are required because the current correlation function is highly oscillatory. The MD results for σ at various electric fields is shown in Fig. 4. The electrical conductivity σ shows an approximately linear trend up to 500 MV/m, then σ increases rapidly beyond it. It implies that the force (F_{el}) on ions from the electric field substantially affects the structural and transport properties, when the electric field is larger than 500 MV/m. As seen from Table 3, the simulated ionic conductivity is close to the experimental value. The fact that fairly reasonable agreement with experiments both D and σ supports our potential model to discuss transport properties in $CaSiO_3$ melt.

According to fluctuation theory, the infrared absorption $\alpha(\omega)$ can be obtained by Fourier transformation of the dipole correlation function $M_{\mathrm{d}}(t) = \sum_i q_i r_i$. It is defined as[13]

$$\alpha(\omega) = \frac{2\pi\omega^2}{3cnVk_{\mathrm{B}}T}\int \langle M_{\mathrm{d}}(0)M_{\mathrm{d}}(t)\rangle \exp(-\mathrm{i}\omega t)\mathrm{d}t, \tag{10}$$

where c, n and V are the velocity of light, the refractive index and the system volume, respectively. This equation can be rewritten by the correlation function of current $C_{ZZ}(t)$ (Ref. 14)

$$\alpha(\omega) = \frac{\langle C_{ZZ}(0)^2\rangle}{3Vk_{\mathrm{B}}T}\int J_Z(t)\exp(\mathrm{i}\omega t)\mathrm{d}t = \frac{4\pi}{cn}\sigma(\omega). \tag{11}$$

The bulk conductivity of the melt corresponds to the $\omega \to 0$ limit of this function, while the infrared absorption spectrum is related to the frequency-dependent quantity. The correlation function $J_Z(t)$ was calculated within a period time of 20 ps, and the Blackman windows were used before Fourier transformation. The frequency-dependent electrical conductivity is shown in Fig. 5.

There are two bands in Fig. 5. These are about 15.873 THz($\sim$529 cm^{-1}) and 24.645 THz ($\sim$821.5 cm^{-1}). When the electric field increases, the intensity of the first band tends to decrease, but the second band becomes broader and has an increase in intensity. Maeda *et al.* have measured the infrared emission spectra of molten $CaO-CaF_2-SiO_2$ by combining hot thermocouple technique and FT-IR,[15] and they have observed a band with main peak 830 cm^{-1} when the molar fraction ratio ($X_{\mathrm{CaO}}/X_{\mathrm{CaF_2}}$) is high.

In summary, we have performed the molecular dynamics simulation for $CaSiO_3$ melt under an electric field, by adopting the effective pair potential with physically reasonable value for the interaction parameters. In fact, for $CaSiO_3$ melt without the electric field our results for the partial radial distribution function, self-diffusion coefficient and electrical conductivity are well compared with experimental results. It is found by applying the electric field that its value as large as 500 MV/m produces great changes in the transport properties ion for the system under consideration. The frequency-dependent electrical conductivity is also calculated, and it is found as partially consistent with experiments.

REFERENCES

1 Y. Waseda and T. M. Toguri, *Material Science of the Earth Interior* (Sci. Pub. Company, Tokyo, 1989).
2 J. E. Enderly, *Amorphous Solids and the Liquid State*, edited by N. H. Mrach, R. A. Street, M. P. Tosi (Plenum Press, New York, 1985).
3 ZHANG Yong-Hong and HUANG Shi-Ping, Chin. Phys. Lett. 16(1999) 253.
4 Huang Shi Ping and F. Yoshida, J. Phys. Soc. Jpn. 66(1997) 392.
5 Huang Shi Ping and F. Yoshida, J. Phys. Soc. Jpn. 66(1997) 1356.
6 Shi Ping Huang, F. Yoshida, Jinglin You, Guochang Jiang and Kuangdi Xu, J. Phys.: Condens Matter, 11 (1999) 5429.
7 M. Matsui, Phys. Chem. Min. 16 (1988) 234.
8 M. Hemmati, A. Chizmeshya, H. W. George C. A. Angell, Phys. Rev. B 51 (1995) 14841.
9 H. Keller, K. Schwerdtfeger, H. Petri, R. Holzle and K. Hennesen, Metall. Trans. B 13 (1982) 237.
10 H. Keller, K. Schwerdtfeger and K. Hennesen, Metall. Trans. B 10 (1979) 1356.
11 J. P. Hansen and I. R. McDonald, The Theory of Simple Liquid (Academic Press, London, 1986).
12 WANG Zuo-wei, LIN Zhi-fang and TAO Rui-bao, Chin. Phys. Lett. 14 (1997) 151.
13 T. Kato, K. Machida, M. Oobatake and S. Hayashi, J. Chem. Phys. 92 (1990) 5506.
14 ZONG Xiang-fu, WANG Xu, WENG Yu-min, YAN Renjin, TANG Guo-an and ZHANG Zhao-qiang, Chin. Phys. Lett. 15 (1998) 767.
15 M. Maeda, Y. Kariya and T. Ikeda, Proceedings of the 5th International Conference on Molten Slags, Fluxes and Slats'97 (1997) 423.